Phosphorous dynamics in soil and dust: a XANES application

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Forcings









Responses

- JEDI in the academy
- Biogeochemical cycles of C (and PyC), N, P
- Vertical and lateral transport of soil and SOM , and terrestrial → aquatic)
- Nano-(bio)geochemistry
- Political ecology. Sustainability use of soil resource, Soil – society relations

Spatial scales: nano to catchment Temporal scales: <minutes to >1000s of years



Outline

- P speciation in soil
 - Effects of climate and soil weathering
- P in Dust
 - Composition and bioavailability
- Concluding thoughts



Biogeochemistry Ρ

- P is an important macronutrient
 - Cellular and genetic processes, energy transfer, structural support of plants
- Apatite **Particulate Matter** Mixed composition Weathering Deposition **Mineral Surfaces and Secondary Compounds Desorption & Dissolution** Plant (Po) **Soil Solution** Uptake (Pi and Po) Monoesters, Orthophosphate Clays, Fe and Al oxides, $(H_2PO_4^- \text{ and } HPO_4^{-2})$ Sorption & Precipitation diesters, Mineralization carbonates, Ca/Fe/Al phosphonates phosphates Immobilization Mineralization Erosion & Leaching P biogeochemical cycle is complex and intrinsically related to soil development **Microbial** (Po) All P originates from Monoesters, diesters, parent material phosphonates, pyrophosphate

Primary Mineral (Pi)

No biological fixation-• > ultimately limiting nutrient

Barnes et al. (In Prep) [Based on Kruse et al., 2015; Tiessen et al., 1984; Walbridge et al., 1991; Tiessen and Moir, 1993]



Global Nutrient Limitation

- Nitrogen and Phosphorus limit net primary productivity (photosynthesis) and terrestrial sequestration of atmospheric carbon dioxide.
 - global climate change concerns



Wieder et al. (2015) model projections of terrestrial C storage where the black line represents <u>no nutrient limitation</u>, red is <u>N inputs</u>, and blue is <u>N+P inputs</u>.



P XANES for soil, sediment, dust

Possible pathways for phosphorus misquantification by sequential extraction



Environmental Science & Technology



Figure 1. Flow chart for modified Hedley fractionations combined with phosphorus K-edge X-ray absorption near-edge structure (XANES) spectroscopic analysis.



Reference P XANES spectra

• Advantages:

- Allows identification and quantification of different P pools: (Fe+Al)-P, Ca-P & organic P
- In situ, non-destructive, & minimal sample pretreatment
- Work conducted at the Canadian Light Source and Stanford Linear Accelerator Center



Barnes et al. (In Prep); Gu et al. 2020 ES&T

Linear combination fitting analysis of P XANES spectra

P speciation in soil

- Knowledge gap: Few observations on how P speciation changes along climatic gradients
 - Especially in areas with low P containing parent material and in Mediterranean and arid ecosystems







Barnes et al. (In Prep)

Shifts with soil weathering

• Shift from Ca to Fe and Al associated P





New conceptual model for soil P dynamics

- Traditional model (Walker & Syers 1976)
 - P biogeochemistry is related to pedogenesis

Primary mineral P Ccluded P Cocluded P Soil organic P Plant P

Time ->

- P stock does not follow W&S
 - Deeper profiles in more weathered soil = greater stock
- P speciation follows W&S
 - Shift from Ca-P to Al/Fe- P with relatively small changes in climate
 - Little impact on Po in these moderately weathered soils





Wind erosion \rightarrow Dust/Atmospheric particulate matter

- ... towards inferring fate of nutrients in dust and implications for biogeochemical cycling of essential elements in the terrestrial ecosystem
- Dust can outpace bedrock nutrient supply over the short term in soils where P concentration in bedrock is low and/or erosion and weathering rates are slow (Aciego et al. 2017)
- Plants utilize PM derived P (Arvin et al. 2017)

Model of dust deposition since Last Glacial Maximum (Albani et al., 2014)



Dust Deposition (g/m²/yr)				
0	0.05	0.5	5	50



Source of dust to W. US soils





Seasonal difference in CO
52% - 59% Asian source: CO (wet - winter, spring)
0 - 37% of Asian source: CO (dry - fall)

Elevational difference in CA

- 12 38% of Asian source: CA high (dry fall)
- 14 22% Asian source: CA low (dry fall)



O'Day et al. 2020 ES&T

K-edge XANES: composition of bulk PM samples

 Organic P species dominant in dust collected from highelevations in both the Sierra and Rockies





Summary

XANES along with traditional soil science and geochemistry methods:

- Acurate representation of P extracted with sequential fractionations
- Determine how P speciation evolves during soil weathering
- Dust inputs are significant sources of plant-available nutrients, esp. in temperate forests
- Dust sources change seasonally (CO) and based on elevation (CA),
- Organic P species dominate PM samples collected from both California and Colorado high elevation systems
- Inorganic P species were prominent in the low elevation (California) site with calcium hydroxyapatite being the most dominant species (Ca abundance suggesting higher contribution of drier areas)



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